Bipolar Copoly(aryl ether) Containing Distyrylbenzene, Triphenylamine, and 1,2,4-Triazole Moieties: Synthesis and Optoelectronic Properties

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ABSTRACT: A novel copoly(aryl ether) (P1) consisting of alternate emitting segments (distyrylbenzene) and a bipolar moiety composed of directly linked electron-transporting aromatic 1,2,4-triazole and hole-transporting triphenylamine was synthesized. The copoly(aryl ether) is readily soluble in common organic solvents and exhibit good thermal stability with thermal decomposition temperature above 450 °C. The emission and the photoluminescence quantum yield of the copolymer are dominated by the emitting segments (distyrylbenzene) with longer emissive wavelength. Electron affinity of P1 is evidently enhanced after introducing the isolated bipolar unit, as confirmed by the lowered lowest unoccupied molecular orbital level (-2.77 eV) relative to PO without bipolar unit (-2.34 eV). This results in improved emission efficiency of its polymer light-emitting diode (indium tin oxide/ poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate)/P1/

INTRODUCTION Since the first discovery of polymeric lightemitting diodes (PLEDs) using poly(*p*-phenylene vinylene) (PPV) as an emitting layer in 1990,¹ PLEDs have attracted much research interest because of their potential applications in large area display and solid-state lighting.² Polymeric materials possess many advantages owing to their solubility and good film-forming properties, rendering them suitable for solution processes such as facile fabrication via spin coating or inkjet printing,^{3,4} and susceptible to structural modification. For high luminescence efficiency to be achieved, it is not only necessary to balance injection and transport between electrons and holes but also important to decrease the energy barriers of charges injection from the opposite electrodes.⁵ However, electron injection is usually more difficult than hole injection in PPV-based conjugated polymers leading to imbalanced charges injection and transport, which greatly reduces the luminescence efficiency of their PLEDs.⁶⁻¹⁰ Two strategies have been attempted to balance charges injection and transport, which is crucial in obtaining efficient electroluminescent (EL) devices. One is to insert an additional electron injection/ transport layer between the emitter and the cathode.¹¹⁻¹³ Nonetheless, fabrication of the multilayer device from polymers, typically deposited by spin coating, is usually a difficult LiF/Ca/Al) due to more balanced charges injection and transport. Blending **P1** with poly(9,9-dihexylfluorene) (**PF**) further improves the efficiency of the device; the best performance was obtained for **PF/P1** = 20/0.8 (w/w) with maximum luminance and maximum luminance efficiency being significantly enhanced to 3260 cd/m² and 1.08 cd/A, respectively, from 380 cd/m² and 0.009 cd/A of **P1**-based device. These results demonstrate that the bipolar moiety can be used to enhance charges injection and transport of electroluminescent polymers. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 3099–3108, 2011

KEYWORDS: bipolar; conjugated polymers; copoly(aryl ether); distyrylbenzene; light-emitting diodes (LED); luminescence; triazole; triphenylamine

task when the solution of a subsequent electron injection/ transport layer will damage the previously coated lightemitting layer. Consequently, single-layer devices are highly preferred from the viewpoints of process simplicity and cost effectiveness.

Another strategy is to fabricate single-layer LEDs that blend charge injection/transport molecules such as oxadiazole, 1,2,4-triazole, triphenylamine (TPA) or carbazole derivatives. Nevertheless, the drawback of this strategy is the crystallization-induced degradation and thermal breakdown of the small molecules during device operation, which unavoidably lead to low emission efficiency and poor stability if their glass transition temperatures (T_g) are low.¹⁴⁻¹⁶ Therefore, the development of emitting copolymers chemically bonded with both electron and hole injection/transport moieties is an ideal strategy in material design of PLEDs. Several research groups prepared copolymers carrying both electron- and hole-transporting moieties in an attempt to improve their device performance.¹⁷⁻²³ Song et al.^{17(e)} synthesized a copolymer containing both carbazole and oxadiazole units; it exhibited 36 times higher EL quantum efficiency as compared to PPV. Li et al.^{18(c)} synthesized a copolymer with both electron-

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withdrawing cyano and electron-rich TPA groups to enhance performance of PPV-based device. Zhang et al.^{19(d)} synthesized an EL polymer containing hole-deficient TPA and electron-deficient oxadiazole to enhance performance of PPV-based device, with a maximum luminescent efficiency of 0.65 cd/A and a maximum brightness of 2100 cd/m². Wu et al.^{20(a)} synthesized a fluorene-based copolymer containing TPA moieties and oxadiazole pendent groups; an organic light-emitting device with this copolymer as the emitting layer exhibited maximum brightness and luminance efficiency of 7128 cd/m² and 2.07 cd/A, respectively.

TPA and its derivatives have attracted considerable interest as hole-transporting materials for use in organic EL devices due to their relatively high hole mobility and low ionization potentials.²⁴ On the contrary, aromatic 1,2,4-triazole and related derivatives are electron-deficient materials, which possess good thermal and chemical stabilities, leading to their common use as electron-transport and hole-blocking materials in LEDs.^{14,25,26} They are two commonly used hole and electron transporters, respectively, in organic and polymeric light-emitting diodes. In general, hole- and electrontransporting materials also demonstrate simultaneously enhanced hole and electron injection, respectively.

In this study, we synthesized a novel copoly(aryl ether) (P1) consisting of alternate light-emitting segment (distyrylbenzene derivatives) and bipolar moiety. The bipolar moiety comprises directly linked hole-transporting TPA and electron-transporting aromatic 1,2,4-triazole. The copoly(aryl ether) exhibits not only good thermal stability but also balanced hole and electron transport relative to homo-poly(aryl ether) (P0) due to the presence of the bipolar moieties. Moreover, the aryl ether functional group was introduced to enhance its solubility in common organic solvents. Finally, to reduce the barrier height for electron (0.4 eV) between emitting distyrylbenzene segments and bipolar moiety, P1 was blended with poly(9,9-dihexylfluorene) (PF) and used as emitting layer. The blending effectively improved the balance between holes and electrons injection, resulting in greatly enhanced maximum luminance and maximum luminance efficiency. These results reveal that the bipolar copoly(aryl ether) (P1) is applicable as emitting dopant; it is also effective in balancing charges injection and transport.

EXPERIMENTAL

Measurements

All newly synthesized compounds were identified by NMR spectra, Fourier transform infrared (FTIR) spectra, and elemental analysis. ¹H NMR and ¹³C NMR spectra were obtained on a Bruker AMX-400 MHz or an AV500 MHz FT-NMR spectrometer, with the chemical shifts reported in ppm using tetramethylsilane as an internal standard. The FTIR spectra were measured as KBr disk on a FTIR spectrometer, model 7850 from Jasco. Elemental analyzer. The weight-average molecular weight (M_w) and polydispersity index (PDI) of polymers were measured with a gel permeation chromatograph (GPC), using tetrahydrofuran (THF) as eluent and monodisperse polystyrenes as

calibration standards. The thermogravimetric analysis (TGA) of polymers was performed under nitrogen atmosphere at a heating rate of 20 °C/min, using a PerkinElmer TGA-7 thermal analyzer. Thermal transition properties of polymers were investigated using a differential scanning calorimeter (DSC), PerkinElmer DSC 7, under nitrogen atmosphere at a heating rate of 10 °C/min. Absorption and photoluminescence (PL) spectra were measured with a Jasco V-550 spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. Cyclic voltammograms were recorded with a voltammetric analyzer (model CV-50W from Bioanalytical Systems) at room temperature under nitrogen atmosphere. The measuring cell consisted of a polymercoated glassy carbon as the working electrode, an Ag/AgCl electrode as the reference electrode, and a platinum wire as the auxiliary electrode. The electrodes were immersed in acetonitrile containing 0.1 M (n-Bu)₄NClO₄ as electrolyte. The energy levels were calculated from onset oxidation or onset reduction potentials $[E_{HOMO} = -(E_{ox,FOC} + 4.8) \text{ eV}; E_{LUMO} =$ $-(E_{\rm red,FOC} + 4.8)$ eV], using ferrocene (FOC) as standard $(-4.8 \text{ eV with respect to vacuum level}).^{27}$

Materials

4-Fluorobenzoyl chloride (TCI), hydrazine monohydrate (Showa), phosphorus pentachloride (PCl₅; Riedel-dehaen), diphenylamine (Fluka), 4-fluoronitrobenzene (Acros), palladium on activated carbon (Pd/C; Aldrich), 1-bromohexane (Acros), hydroguinone (Lancaster), iodine (I₂; Riedeldehäen), iodic acid (HIO3; Lancaster), 4-acetoxystyrene (Aldrich), palladium (Pd) acetate (Acros), triethylamine (Merck), tri-(o-toly)phosphine (Acros), phenol (Merck), N,Ndimethyaniline (Acros), 1,3-dimethyl-3,4,5,6-tetrahydro-2-(1H)-pyrimidinone (DMPU; Alfa), dimethyl sulfoxide (DMSO; Tedia), N,N-dimethylformamide (DMF; Tedia), chloroform (CHCl₃) (Tedia). THF (Tedia), and other solvents were from commercial source and used without purification. 1,2-Bis (chloro(4-fluorophenyl)methylene)hydrazine (4) was prepared from 4-fluorobenzoyl chloride by reacting consecutively with hydrazine monohydrate and PCl₅ (Scheme 1). N', N'-Diphenylbenzene-1,4-diamine (8) was synthesized from diphenylamine (5) and 1-fluoro-4-nitrobenzene (6) to obtain *N*-(4-nitrophenyl)-*N*-phenylbenzenamine (7), followed by reduction with hydrazine monohydrate. The synthesis of monomers M2 and 15 were reported previously.²⁸

Synthesis of 3,5-Bis(4-fluorophenyl)-4triphenylamine-1,2,4-triazole (9)

To a 100-mL two-necked glass reactor, **4** (0.10 g, 3 mmol), **8** (0.84 g, 3 mmol), and DMF (50 mL) were added. The mixture was stirred at 135 °C for 24 h under a nitrogen atmosphere. The precipitates, obtained after pouring the mixture into aqueous solution of HCl (500 mL, 3 N), were collected, dried, and recrystallized from ethanol to provide white sheet-like crystals of **9** (59%).

mp > 240 °C ¹H NMR (CDCl₃, ppm): δ 7.5–7.47 (m, 4H), 7.33 (t, J = 8.6 Hz, 4H), 7.26 (t, J = 8.6 Hz, 4H), 7.23–7.21 (d, J = 8.7 Hz, 2H), 7.10 (t, J = 8.4 Hz, 2H), 7.04–7.02 (d, J = 8.0 Hz, 4H), 6.90–6.88 (d, J = 8.8 Hz, 2H). FTIR (KBr, pellet,







9, bipolar model M1 and emitting model M2 and emitting monomer 15.

cm⁻¹): v 1512 (C=N), 1093 (C-F). Anal. Calcd. (%) for: C32H22F2N4: C, 76.79; H, 4.43; N, 11.19. Found: C, 76.72; H, 4.51; N, 11.23.

Synthesis of N-(4-(3,5-Bis(4-phenoxyphenyl)-4H-1,2,4triazol-4-yl)phenyl)-*N*-phenylbenzenamine (M1)

A mixture of 9 (0.391 g, 1.5 mmol), phenol (0.298 g, 3.15 mmol), K₂CO₃ (0.442 g, 3.2 mmol), and 6 mL of DMF was stirred at 160 °C for 20 h under a nitrogen atmosphere

(Scheme 1). The mixture was precipitated from distilled water; the precipitates were collected by filtration, dried in vacuo, and recrystallized from ethanol to afford M1 (83%). mp >240 °C. ¹H NMR (CDCl₃, ppm): δ 7.5–7.47 (m, 8H), 7.35-7.32 (m, 4H), 7.29-7.25 (m, 4H), 7.23 (m, 2H), 7.12-7.09 (m, 8H), 7.04 (m, 4H), 6.90 (m, 2H). FTIR (KBr, pellet, cm⁻¹): v 1509 (C=N), 1264 (C-N), 1232 (C-O-C). Anal. Calcd. (%) for: $C_{44}H_{32}N_4O_2$: C, 81.46; H, 4.97; N, 8.64. Found: C, 81.24; H, 5.00; N, 8.60.



SCHEME 2 Synthesis of bipolar copoly (aryl ether) (**P1**) and poly(aryl ether) (**P0**).

Synthesis of Bipolar Copoly(aryl ether) (P1) and Poly(aryl ether) (P0)

Bipolar copoly(aryl ether) (P1) and poly(aryl ether) (P0) were prepared simultaneously for comparative study. The poly(aryl ether)s P1 or P0 were prepared from bisphenol (15) and bipolar monomer (9) or dibromo monomer (16), respectively, as shown in Scheme 2. A two-necked glass reactor was charged with monomers (16 or 9; 0.50 mmol), bisphenol 15 (0.50 mmol), 10 mL of toluene, 5 mL of DMPU, and an excess of K_2CO_3 (0.166 g, 1.20 mmol). The mixture was stirred at 160 °C for 48 h (P0) or 24 h (P1). After removal of toluene, the reaction mixture was first diluted with 2 mL of *N*-methylpyrrolidone and then dropped into 250 mL of a mixture of methanol and distilled water (v/v = 9/1). The appearing precipitates were collected by filtration and further purified by extraction with isopropyl alcohol for 24 h using a Soxhlet extractor.

P0: 15 (0.258 g, 0.5 mmol) and **16** (0.132 g, 0.5 mmol). ¹H NMR (CDCl₃, ppm): δ 7.45 (m, 8H), 7.27 (m, 4H), 7.06–6.88 (m, 8H), 5.06 (s, 4H), 4.01 (m, 4H), 1.83–1.49 (m, 12H), 1.33 (m, 4H), 0.88 (m, 6H). FTIR (KBr, pellet, cm⁻¹): ν 1240 (C=O=C), 968 (C=C). Anal. Calcd. (%) for **P0**: C, 81.78; H, 7.84. Found: C, 80.74; H, 7.69.

P1: 15 (0.258 g, 0.5 mmol) and **9** (0.250 g, 0.5 mmol). ¹H NMR (CDCl₃, ppm): δ 7.5–7.47 (m, 4H), 7.35–7.32 (m, 4H), 7.32–7.28 (m, 8H), 7.23–7.20 (m, 8H), 7.12–7.09 (m, 2H), 7.04 (m, 4H), 6.90 (m, 2H) 6.76 (m, 4H), 4.03 (m, 4H), 1.78 (m, 4H), 1.50 (m, 4H), 1.34 (m, 8H), 0.87 (m, 6H). FTIR (KBr,

pellet, cm⁻¹): v 1598 (—C=N—), 1240 (C—O—C), 964 (C=C). Anal. Calcd. (%) for **P1**: C, 81.28; H, 6.80; N, 5.67. Found: C, 79.34; H, 6.41; N, 5.83.

Fabrication of Polymer Light-Emitting Diodes

To evaluate the applicability of the bipolar copoly(aryl ether) (P1) in enhancing emission efficiency, double-layer PLEDs [indium tin oxide/poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (ITO/PEDOT:PSS)/polymer/Ca/Al] were fabricated by the solution process. First, a transparent ITO glass substrate was successively cleaned with neutraler reiniger/deionized water (v/v = 1/3) mixture, deionized water, acetone, and 2-propanol using an ultrasonic bath, and then dried in vacuo overnight. Aqueous dispersion of PEDOT:PSS was immediately spin coated on top of the cleaned ITO glass as hole-injection layer and dried at 150 °C for 15 min. Emitting layer was then deposited by spin coating (1000 rpm) onto the PEDOT:PSS layer from a polymer solution in 1,2dichlorobenzene (10 mg/mL). Finally, calcium and aluminum were consecutively vacuum deposited as cathodes using a vacuum coater at a pressure of 2 $\,\times\,$ 10^{-6} Torr. Luminance versus voltage and current density versus voltage characteristics of the devices were measured using a combination of a Keithley power source (model 2400) and an Ocean Optics USB2000 fluorescence spectrophotometer. The optoelectronic measurements were conducted in a glove box filled with nitrogen to avoid possible degradation under device operation.

 TABLE 1 Polymerization Results and Characterization of Polymers

| Polymer | Yield (%) | <i>M</i> _n ^a (×10 ⁴) | <i>M</i> _w ^a (×10 ⁴) | PDI ^a | Т _g ь (°С) | <i>T</i> d [°] (°C) |
|---------|--------------|---|---|------------------|--------------------------|---------------------------------|
| P0 | 79 | 2.74 | 8.49 | 3.10 | 136 | 389 |
| P1 | 98 | 1.35 | 2.05 | 1.52 | - | 450 |

 $^{\rm a}$ $M_{\rm n},$ $M_{\rm w},$ and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards in THF.

 $^{\rm b}$ Glass transition temperature was measured by DSC at a scan rate of 20 °C/min under nitrogen. The glass transition temperature of **P1** was not detectable up to 300 °C.

^c The temperature at 5 wt % loss under nitrogen atmosphere.

RESULTS AND DISCUSSION

Characterization of Bipolar Monomer (9) and Model (M1) and Copoly(aryl ether) (P1) and Poly(aryl ether) (P0)

In this study, difluoro bipolar monomer (9), with directly linked TPA and 1,2,4-triazole as core, was used to synthesize bipolar copoly(aryl ether) (P1). N-(4-(3,5-Bis(4-fluoro-phenyl)-4H-1,2,4-triazol-4-yl)phenyl)-N-phenylbenzenamine (9) and N-(4-(3,5-bis(4-phenoxyphenyl)-4H-1,2,4-triazol-4-yl)



FIGURE 1 Absorption and PL spectra of **M1**, **M2**, **P1**, and **P0**: (a) in THF (10^{-5} M; $\lambda_{ex} = 308$ nm for **M1**, 331 nm for **M2**, 401 nm for **P0**, and 403 nm for **P1**); (b) in film state ($\lambda_{ex} = 402$ nm for **P0** and 413 nm for **P1**) and PL spectrum of **PF** in film state. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

phenyl)-*N*-phenylbenzenamine (**M1**) containing bipolar moieties were synthesized according to the synthetic routes outlined in Scheme 1.^{23(a),28(b)} The ¹H NMR spectra of **P0** and **P1** are shown in Supporting Information Figure. S1. The main ¹H NMR spectral difference between **P0** and **P1** lies in chemical shift regions at 6.7–7.7 ppm, which originate from incorporated bipolar residues. Bipolar copoly(aryl ether) (**P1**) and poly(aryl ether) (**P0**) were synthesized by the nucleophilic displacement reaction of 1,4-bis(4-hydroxystyryl)-2,5-dihexyloxyphenylene (**15**) with functionalized aromatic monomers **9** and **16**, respectively (Scheme 2).

The poly(aryl ether)s (P0 and P1) are readily soluble in common organic solvents such as toluene, chloroform, chlorobenzene, and THF. The weight-average molecular weights $(M_{\rm w})$ of **P0** and **P1** are 8.49 \times 10⁴ and 2.05 \times 10⁴, respectively, with PDIs being 3.10 and 1.52 (Table 1), as determined by GPC using monodisperse polystyrenes as calibration standards. Clearly, the $M_{\rm w}$ of **P1** is much lower than that of P0. This has been attributed to reduced reactivity of bipolar monomer 9 than 1,4-bis(bromomethyl)benzene (16) due to its steric hindrance and electron-deficient characteristic. The $T_{\rm g}$ of **P0** was 136 °C, as determined from the second heating DSC scans, while no noticeable T_{g} was observed for P1 (Supporting Information Fig. S2). Thermal decomposition temperatures (T_d : at 5 wt % loss) of the poly(aryl ether)s were evaluated with TGA. The residual weights at 800 °C of both P0 and P1 were above 30% under nitrogen atmosphere (Supporting Information Fig. S3). Moreover, the T_d of P0 and P1 were 389 and 450 °C (Table 1), respectively, indicating that their thermal stability is above moderate.

Photophysical Properties of Bipolar Copoly(aryl ether) (P1) and Poly(aryl ether) (P0)

Optical properties of the poly(aryl ether)s were investigated by absorption and PL spectra, both in solution and film states, to evaluate the influence of the bipolar groups. Figure 1 illustrates the absorption and PL spectra of **M1**, **M2**, **P0**, and **P1** in CHCl₃ and those of **P0** and **P1** films, with the characteristic optical data summarized in Table 2. The absorption maximum of bipolar model **M1** in CHCl₃ appears at 308 nm, whereas those of fluorophore model **M2**, **P0**,

| IADLE 2 Optical Properties of WI , WZ , PU , and |
|--|
|--|

| Molecule/ Polymer | UV–Vis λ_{max} Solution (nm) ^a | UV–Vis λ _{max} Film (nm) | PL λ _{max} Solution (nm) ^b | PL λ _{max} Film (nm) ^b | Φ_{PL}^{c} |
|----------------------|---|--------------------------------------|--|--|-----------------|
| M1 | 308 | - | 390 | - | 0.71 |
| M2 | 331, 397 | - | 445, 463s | - | 0.57 |
| P0 | 335, 401 | 337, 402 | 446, 470s | 486, 510s | 0.53 |
| P1 | 310, 403 | 319, 413 | 448, 471s | 488s, 514 | 0.54 |

 a In THF (1 \times 10 $^{-5}$ M).

^b s: Wavelength of shoulder.

 c Φ_{PL} : quantum yield determined in CHCl₃, relative to quinine sulfate in 1 N H₂SO_{4(aq)} at a concentration of 10⁻⁵ M ($\Phi_{PL}=0.55$).



FIGURE 2 Cyclic voltammograms of M1, P0, and P1 coated on glassy carbon electrode; scan rate: 100 mV/s.

and P1 are around 397-403 nm. The main absorption bands around 397–403 nm can be attributed to the π - π * transitions of distyrylbenzene derivatives in M2, P0, and P1. Both emitting segments (distyrylbenzene derivatives) and bipolar residues contribute to the absorption spectrum of **P1**, which are comparable to the absorption spectra of model compounds. For instance, the longer major absorption of P1 (\sim 403 nm) can be attributed to emitting segments (M2 residues), whereas the shorter wavelength absorption (ca. 310 nm) has definitely originated from bipolar M1 residues. Solid-state absorption maxima of P0 and P1 are slightly red shifted (1-10 nm) relative to solution state ones, originating in aggregate formation via intrachain or interchain interactions.

Similarly, P0 and P1 exhibit major PL peaks at 486-514 nm in solid state which are red shifted about 40-43 nm relative to those in solution state (Table 2), implying the formation of aggregate in film state. Moreover, the PL spectra of P1 were almost identical whether they were excited with 308 nm (major absorption of bipolar model M1) or 402 nm (major absorption of emitting M2), suggesting efficient Förster energy transfer from bipolar residues to emitting segments (distyrylbenzene derivatives) under the photoexcitations. Partial overlap between emission spectrum of bipolar M1 and absorption spectrum of P0 contributes greatly to the energy transfer.^{18(e),20,21(a)} In addition, it is noteworthy that the emission spectrum of PF partially overlaps with the absorption spectra of PO-P1 (Fig. 1), indicating that energy transfer from PF to PO-P1 can be expected as well. Based on this characteristic, efficient PLEDs were obtained using blends of PO-P1 and PF as emitting layer, which will be discussed later. The PL quantum yields (Φ_{PL}) of M1, M2, P0, and **P1** in THF (at a concentration of 10^{-5} M) are 0.71, 0.57, 0.53, and 0.54, respectively. The $\Phi_{PL}s$ of **P0** and **P1** are almost the same and close to that of M2, suggesting that they are mainly determined by the emitting segments (distyrylbenzene derivatives).^{28(a)}

Electrochemical Investigations

Hole and electron affinities of M1, P0, and P1 were evaluated by their onset oxidation and reduction potentials determined by electrochemical methods. Their cyclic voltammograms (CVs) were first measured to investigate the electrochemical properties. The highest (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were estimated by the equations: E_{HOMO} (eV) = -($E_{\text{ox,FOC}}$ + 4.8) and $E_{\rm LUMO}$ (eV) = -($E_{\rm red,FOC}$ + 4.8), where $E_{\rm ox,FOC}$ and $E_{\rm red,FOC}$ are the onset oxidation and reduction potentials, respectively, with respect to the FOC/ferrocenium couple. The CVs are shown in Figure 2, with the representative electrochemical data summarized in Table 3. In this study, copoly(aryl ether) (P1) contains bipolar residues derived from electron-transporting triazole and hole-transporting TPA. The estimated HOMO energy levels of M1, P0, and P1 are -5.35, -5.30, and -5.32 eV, whereas the estimated LUMO levels are -2.74, -2.34, and -2.77 eV, respectively. In addition, the HOMO and LUMO energy levels of M2 should be close to -5.15 and -2.59 eV, respectively, of our previous polymer,²⁹ because they possess the same distyrylbenzene residue. The HOMO level of P1 (-5.32 eV) is almost equal to that of P0 (-5.30 eV) after incorporating the bipolar residues, suggesting that holes are mostly injected into the emitting segments (M2 residues). However, the LUMO level of P1 (-2.77 eV) is much lower than that of P0 (-2.34 eV) after introducing the bipolar residues, meaning that energy barrier of electron injection from cathode is lower for P1. Therefore, electron affinity of P1 is enhanced due to the incorporation of the bipolar residues, resulting in improved balance in charges injection and transport. Moreover, the LUMO level of PF (-2.53 eV) lies between those of P0 (-2.34 eV) and bipolar M1 (-2.74 eV). Accordingly, blending P1 with PF will enhance electron transport from the bipolar residues to emitting segments (distyrylbenzene derivatives). This might be an effective strategy to improve balance in charges injection and transport for P1 and enhance charges recombination in emitting segments.

Electroluminescent Properties of Bipolar Copoly(aryl ether) (P1) and Poly(aryl ether) (P0)

Double-layer PLEDs [ITO/PEDOT:PSS/P1 or P0/LiF(0.5 nm)/ Ca(50 nm)/Al (100 nm)] were fabricated to investigate their device performances. Figure 3 shows the current density and luminance versus bias characteristics of the EL devices, with

| TABLE 3 | Electrochemical | Properties o | of M1, P0 , and | d P1 |
|---------|-----------------|--------------|------------------------|------|
|---------|-----------------|--------------|------------------------|------|

| Molecule/ Polymer | E _{ox} versus FOC (V) ^a | E _{red} versus FOC (V) ^a | Е _{номо} (eV) ^b | Е _{LUMO} (eV) ^b | Eg ^{el} (eV) ^c |
|----------------------|---|--|--|--|------------------------------------|
| M1 | 0.55 | -2.06 | -5.35 | -2.74 | 2.61 |
| P0 | 0.50 | -2.46 | -5.30 | -2.34 | 2.96 |
| P1 | 0.52 | -2.03 | -5.32 | -2.77 | 2.55 |

^a $E_{FOC} = 0.47$ V versus Ag/AgCl.

^c $E_{\text{HOMO}} = -(E_{\text{ox,FOC}} + 4.8) \text{ eV}; E_{\text{LUMO}} = -(E_{\text{red, FOC}} + 4.8) \text{ eV}.$ ^c Electrochemical band gap: $E_{g}^{\text{ el}} = \text{LUMO} - \text{HOMO}.$



FIGURE 3 Brightness versus bias and current density versus bias characteristics of PLEDs using **P0** and **P1** as emitting layer. Device structure: ITO/PEDOT:PSS/**P0** or **P1** (90–110 nm)/LiF(0.5 nm)/Ca(50 nm)/Al(100 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the characteristic performance data summarized in Table 4. The turn-on voltage of P1-based device is 8.9 V, which is much lower than that of PO-based one (17.7 V) This is clearly attributed to the presence of bipolar moieties in P1 that promotes charges injection and transport. Moreover, maximum luminance and maximum luminance efficiency of the **P1**-based device were improved to 380 cd/m^2 and 0.009cd/A, respectively, from 30 cd/m² and 0.001 cd/A of the P0based device. The performance improvement is attributable to more balanced charges injection and transport (Fig. 3). The inferior device performance is probably caused by the high energy barrier for electron transport (0.4 eV), between the emitting segments (distyrylbenzene derivatives) and the bipolar moieties, than that for hole transport (0.05 eV). This leads to imbalance in the charges transport and reduction in the recombination ratio of electrons and holes. Moreover, the

 TABLE 4
 Optoelectronic Performance of Polymer Light-emitting

 Diodes^a
 Polymer Light-emitting

| Emittin Layer Compo (w/w) ^b | ng osition | Turn-on Voltage (V) ^c | Maximum Luminance Efficiency (cd/A) | Maximum Luminance (cd/m ²) | CIE Coordinates (<i>x</i> , <i>y</i>) ^d |
|---|---------------|-------------------------------------|--|--|--|
| PF/P1 | (20/0.2) | 5.5 | 0.72 | 1700 | (0.20, 0.22) |
| PF/P1 | (20/0.4) | 6.0 | 0.88 | 2400 | (0.20, 0.41) |
| PF/P1 | (20/0.8) | 6.2 | 1.08 | 3260 | (0.21, 0.49) |
| PF/P1 | (20/1.6) | 7.2 | 0.61 | 1810 | (0.21, 0.50) |
| P1 | | 8.9 | 0.009 | 380 | (0.21, 0.50) |
| PF | | 5.5 | 0.33 | 1160 | (0.18, 0.18) |
| P0 | | 17.7 | 0.001 | 30 | (0.18, 0.35) |
| PF/P0 | (20/0.8) | 7.2 | 0.49 | 1210 | (0.18, 0.29) |

^a Device structure: ITO/PEDOT:PSS/emitting layer/LiF/Ca/AI.

^b The weight ratios are given in parentheses.

^c The voltage required for the luminance of 10 cd/m².

^d The CIE coordinates at maximum luminance.



FIGURE 4 (a) Brightness versus bias and (b) current density versus bias characteristics of PLEDs using blends of **PF** and **P1** (0–1.6 mg) as emitting layer. Device structure: ITO/PEDOT:PSS/ **PF** + **P1** (90–110 nm)/ LiF(0.5 nm)/Ca(50 nm)/Al(100 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

LUMO level of **PF** (-2.53 eV) lies between those of **PO** (-2.34 eV) and bipolar **M1** (-2.74 eV). Accordingly, blending **PF** with **P1** might facilitate electron transport from the bipolar moieties to the emitting segments and thus enhance the device performance.



FIGURE 5 Energy band diagrams of M1, P0, P1, and PF.



FIGURE 6 AFM images of blend films (scan size: $5 \times 5 \mu m^2$): (a) PF/P1 = 20/0.4, RMS roughness = 1.31 nm, (b) PF/P1 = 20/1.6, RMS roughness = 3.38 nm.

Figure 4 shows the current density and luminance versus bias characteristics of the PLEDs using blends of **PF** and **P1** as emitting layer and the representative data are summarized in Table 4. The turn-on voltages were raised from 0.2 mg to 7.2 V when the weights of **P1** were increased from 0.2 mg to 1.6 mg. This is reasonably attributed to the bipolar residues in **P1**, which act as charge trapping center in the blend layer. Because the LUMO and HOMO levels of **P1** are enclosed within those of **PF** (Fig. 5), maximum luminance and maximum luminance efficiency of the blend device (**PF**/**P1** = 20 mg/0.8 mg) were enhanced to 3260 cd/m² and 1.08 cd/A, respectively, superior to those of **P1**-based device. The performance improvement has been ascribed to more balanced charges injection and transport in the blend device. However, further increase in **P1** contents (**PF/P1** = 20 mg/

1.2 PF/P1 (mg / mg) 20/0 1.0 20/02 Nomalized EL Intensity 20/0.4 0.8 20/0.8 20/1.6 0/20 0.6 0.4 0.2 PART CLARK 0.0 400 500 600 700 Wavelength (nm)

FIGURE 7 Emission spectra of PLEDs using blends of **PF** and **P1** as emitting layer. Device structure: ITO/PEDOT:PSS/**PF** + **P1** (90–110 nm)/LiF(0.5 nm)/Ca(50 nm)/Al(100 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1.6 mg) leads to quick performance degradation, suggesting that there exists an optimal content of bipolar residues in balancing the charges injection and transport. Moreover, morphology of active layer also plays role in determining the device performance. The atomic force microscopy (AFM) images of active layer (Fig. 6) can also reasonably explain this performance reversion at higher **P1** contents. The rootmean-square (RMS) surface roughness of the blend films increases drastically from 1.31 nm to 3.38 nm as the **PF/P1** ratio is increased from 20 mg/0.4 mg to 20 mg/1.6 mg. High surface roughness leads to performance degradation of the blend device. Wang and coworkers^{28(c)} prepared two bipolar fluorene-based conjugated copolymers chemically doped with benzothiadiazolyl chromophore, which were applied as emitting layers to obtain a optimal device efficiency of 2.02



FIGURE 8 CIE coordinates of the EL devices (at maximum brightness) based on blends of PF and P1. Device structure: ITO/PEDOT:PSS/PF + P1 (90–110 nm)/LiF(0.5 nm)/Ca(50 nm)/Al(100 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cd/A. However, bipolar copoly(aryl ether) P1 is used as an emitting dopant to enhance device performance by improving balance in charges injection and transport. Moreover, the emitting chromophore in P1 is mainly distyrylbenzene residues (M2 residues). As shown in Figure 7, the emission spectra of blend devices are almost identical with that of P1based device at high P1 content (PF/P1 = 20/0.8 or 20/1.6). Similarly, the 1931 Commission Internationale de l'Eclairage (CIE) coordinates (x, y) of the EL emission shift from (0.20, 0.22) of blend device (PF/P1 = 20/0.2) to (0.21, 0.50) of blend device (**PF**/**P1** = 20/1.6) (Fig. 8, Table 4). Therefore, the device performance of bipolar copoly(aryl ether) P1 can be further enhanced by suitably blending with PF to balance charge injection and transport. The results demonstrate that polymers containing bipolar moieties are effective in manipulating the performance of optoelectronic devices.

CONCLUSIONS

We have successfully synthesized a novel copoly(aryl ether) (P1) consisting of alternate emitting segment (distyrylbenzene derivatives) and bipolar moiety (linked TPA and aromatic 1,2,4-triazole). The copoly(aryl ether) was soluble in common organic solvents and thermally stable (T_d at 5 wt % loss: 450 °C). The PL spectra of P1 were almost identical whether they were excited with 308 nm or 402 nm, because of efficient Förster energy transfer. Estimated HOMO and LUMO levels of bipolar model M1 were -5.35 and -2.74 eV, respectively. The HOMO levels of P0 and P1 were -5.30 and -5.32 eV, respectively, while their LUMO levels were -2.34and -2.77 eV. Maximum luminance and maximum luminance efficiency of P1-based device (380 cd/m², 0.009 cd/A) were superior to those of **P0**-based device (30 cd/m², 0.001 cd/ A). Furthermore, blending the bipolar copoly(aryl ether) (P1) with PF resulted in significant performance enhancement. The performance enhancements had been attributed to improved carriers injection and transport. Blend device $(\mathbf{PF}/\mathbf{P1} = 20/0.8)$ showed the best performance (maximum luminescence efficiency: 1.08 cd/A; maximum luminescence: 3260 cd/m^2). Current results indicate that the bipolar copoly(aryl ether) (P1) is potentially applicable not only as charges injection/transport promoter but also as emitting dopant.

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